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Quantitative determination of surface area of silica gel particles by near infrared spectroscopy and chemometrics

Alfred A. Christy

Department of Chemistry, Faculty of Engineering and Science, University of Agder, Serviceboks 422, N-4604 Kristiansand, Norway

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ABSTRACT

Surface areas of silica gel particles have been quantitatively determined by using near infrared spectrometry and chemometrics. Surface areas of six silica gel samples with varying surface area (300–750 m^2/g) have been determined by the common Brunauer–Emmett–Teller (BET) method and used in preparing mixtures of silica gel samples with varying surface area in the ranges 300–474 and 500–750 m^2/g. The near infrared spectra of the mixtures were measured and the spectral profiles calibrated against the calculated surface area of the mixtures as dependent variable using partial least squares (PLS) technique. The models obtained from the calibrations were then used in predicting the surface area of unknown silica gel samples.

The error estimate in the surface area predicted for the unknown samples lie in the same range as the error limits in the BET surface area determination. The technique provides a fast, easy and inexpensive method for the determination of surface area of silica gel particles.

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1. Introduction

Porous materials are generally characterised by several physical parameters such as porosity, surface area, mean pore size and pore size distribution. Silica gel, the amorphous form of silica is porous and therefore characterised by the same parameters. Amorphous silica is an important material in the field of catalysis, separation science and polymers. In the field of separation science silanol groups in silica gel are chemically modified to give stationary phases with a variety of different functional groups and the concentration of these functional groups on the surface is a measure of the effectivity of a chromatographic column. One of the parameters that are needed for the determination of this stationary phase effectivity is the surface area of the silica gel particles.

The surface areas of silica gel samples are measured by Brunauer–Emmett–Teller (BET) method or by light scattering using a light scattering particle size distribution analyser (LSPDA) [1]. However, the BET method is the most common. The method employs the adsorption of nitrogen at the temperature of liquid nitrogen (77 K). The experimental nitrogen adsorption isotherm for the relative pressures (p/p_0) between 0.05 and 0.35 is fit to a two term BET equation (Eq. (1)) describing a theoretically obtained isotherm for a multilayer nitrogen adsorption.

$$\frac{p}{X_a(p_0 - p)} = \left(\frac{1}{X_m C}\right) + \left\{\frac{(C-1)}{X_m C}\right\}\left(\frac{p_0}{p}\right) \quad (1)$$

X_a is the adsorbed nitrogen in mol/g adsorbant, X_m is the specific monolayer capacity of nitrogen in mol/g adsorbent and C is a constant.

The slope and intercept of the straight line fit of the data are then used to calculate the specific monolayer capacity, X_m. The surface area according to BET (S_{BET}) is then determined by the multiplication of X_m by the cross-sectional area, A_m of a nitrogen molecule and the Avagadros number N (Eq. (2)).

$$S_{BET} = X_m A_m N \times 10^{-18}\ m^2/g \quad (2)$$

The reproducibility of the surface area determined by BET method is around ±5% [1].

Infrared spectroscopy both in the mid-IR region [2–8] and in the near-IR region [9,10] has been extensively used in the study of silica particles. A lot of attention was focused on the study of the silanol groups on the surface.

This is because of the strong absorption bands arising from the OH vibrations. The silanol groups OH stretching vibrations absorb in the region 4000–700 cm^{-1} and the overtones and combination frequencies of the silanol groups absorb in the region 4000–11,000 cm^{-1}. The peak assignments of the absorptions of the surface silanol groups in the mid- and near-infrared region are given in Table 1.

E-mail address: alfred.christy@hia.no.

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Table 1
Mid-IR and NIR band assignments for water adsorbed silica gel samples

Peak (cm^{-1})	Band assignment
3700–3550	OH stretch silanol groups
3400–3500	OH stretch hydrogen bonded silanol groups
4540	Combination band OH stretching and bending silanol groups
5265	Combination band OH stretching and bending water molecules
6800–7300	Overtones of OH stretch silanol groups and hydrogen bonded silanol groups

There have been several reports on the determination of silanol groups using physical and chemical methods [11–14]. Even though, there are differences in the silanol number determined by these methods, there is a general understanding that the concentration of silanol groups on the silica surface is constant.

The silanol groups are polarised and can form hydrogen bondings with molecules that are polar. Water molecules are readily absorbed by silica gel particles because of this nature and silica gel is regarded as one of the best drying agent in industrial applications. When dry silica gel particles are exposed to air, water molecules are adsorbed on to the surface by forming hydrogen bonds with the silanol groups.

The amount of water that is adsorbed is obviously depends on the concentration of silanol groups on the surface. If the concentration of silanol groups, silanol number, is constant then the mass of the water molecules that a silica sample adsorb should be proportional to its surface area. Furthermore, the infrared spectrum of the silica gel sample should contain absorption bands with their intensities of absorptions proportional to the water molecules adsorbed. These facts suggest that the computation of the surface area from the intensity of one of the bands in the infrared spectrum is possible if the concentration of the silanol number and the mass of the water molecules that form a monolayer on the silica gel surface is known. However, the practical approach to do this is rather difficult because of the difficulties in determining the mass of the monomolecular layer of water adsorbed on the silica gel surface from the infrared spectrum.

Another approach to the problem is to find a correlation between the surface area and the infrared spectra of silica gel samples in their hydrated form. The correlation can then be used in determining surface area of an unknown sample. This approach naturally requires a multivariate approach so that a model describing the correlation can be built. The partial least squares (PLS) technique is an excellent tool in this respect and the applications involving partial least squares calibrations are numerous.

The aim of this paper is to demonstrate that the surface area of silica gel particles can be determined with a set of samples with known surface area and their near infrared spectra. This is the first time that such an approach is being reported in the literature.

2. Experimental

2.1. Samples, determination of surface area and preparation of mixtures for analysis

Six silica gel samples with varying surface areas from 300–750 m^2/g were purchased from Sigma Alridch. The determination of surface area of the silica gel samples was carried out by Brunauer, Emmett and Teller (BET) technique with a TriStar 3000 gas adsorption analyser (Micromeritics Instrument Corporation, USA). These six samples were then used to prepare two sets of silica gel samples of varying surface areas. One set of samples containing 17 different mixtures in the range 300–474 m^2/g and the second set of samples containing 30 mixtures in the range 500–750 m^2/g were prepared by weighing different proportions of the six silica gel samples. The total surface area of each of the sample in the glass vial was computed from the weights of the silica sample components in the mixture and their respective surface areas. The calculated BET surface area in m^2/g was then computed using the total area and the total weight of the sample. In addition some independent samples in the regions mentioned above were prepared for the prediction of surface area by mixing samples in different proportions.

All these silica gel samples make the experimental work easy because of their adsorption capabilities of water molecules. They are all with adsorbed water molecular layers and there is no need for hydration of the silica gel samples. The sample mixtures were prepared in glass vials so that the near infrared spectra could be measured directly without transferring the sample to another container.

2.2. Near infrared (NIR) measurements

The near infrared measurements were made using a PerkinElmer Spectrum One NTS FT-NIR spectrometer equipped with a PerkinElmer transflectance accessory and deuterated triglycine sulphate detector. The glass vial containing a sample was placed directly on the crystal of the transflectance accessory and the near infrared spectrum was measured in the region 10,000–4000 cm^{-1} at a resolution of 16 cm^{-1}. A total of 20 scans was made on each sample. The near infrared radiation penetrates through the silica particles, absorbed, reflected and returns back to the instrument and detected. The sample in the glass vial should have an infinite thickness so that the spectrum could be used for quantitative purposes. The sample thickness that arises from the amount of silica particles used in each of the sample is sufficient enough to give an infinite depth of penetration for the infrared radiation. The radiation returning to the instrument is denoted by R and converted to log $(1/R)$ format. This gives near infrared profiles of the samples similar to an absorption spectrum in the mid-infrared region.

2.3. Multivariate calibration and prediction

The near infrared spectral profiles of the calibration samples and prediction samples were imported into SIRIUS program [15] so that the spectral profiles of the mixtures form rows of a calibration matrix (Fig. 1). The near infrared profiles of the samples in log $(1/R)$ format become variables in the data matrix. The mixtures prepared for the calibration sets contain samples with calculated surface areas. The calculated BET surface area of each of the sample is put in a column as its corresponding dependent variable (Fig. 1). The spectral profiles in the data matrix can be subjected to pretreatment before calibration. During calibration, the multivariate data program establishes a model between the spectral profiles or pre-treated data in the data matrix and the BET surface areas in the column containing the dependent variable. The processes involved in the calibration model building and prediction can be found elsewhere [16].

Cross-validated [17] partial least squares calibration models were established between the second derivative profiles of the near infrared spectra of the samples in the calibration sets and their BET surface areas. Cross-validation is used to evaluate the prediction ability of the calibration model in a PLS analysis [16]. This is done by grouping the samples in the calibration set into smaller sets. The sets can contain a few samples each. First, the samples from one of the sets are kept out and a calibration model is built between all the samples in the remaining sets and the dependent variable. This

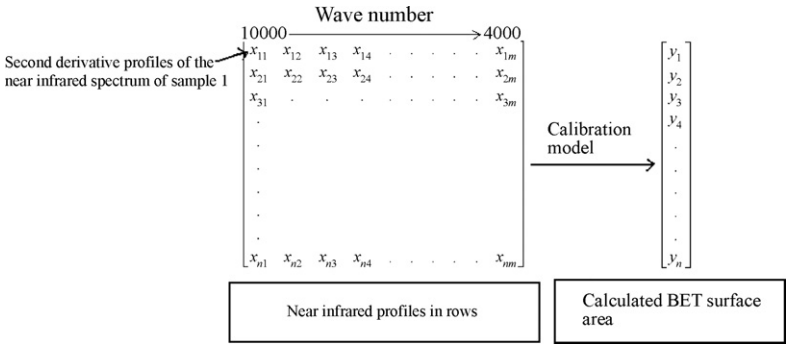

Fig. 1. The matrix arrangement of second derivated near infrared spectral profiles and calculated BET surface area.

calibration model is used to predict the dependent variable of the samples that were kept outside. The process is repeated by keeping out samples from other sets each time. Cross-validation of a calibration model makes it possible to select the optimum number of components or factors, i.e. the number giving the minimum prediction error for the calibration set. The final calibration model is established with the number of components that gives minimum prediction error. This model is then used to predict the dependent variable of the unknown samples in the prediction set.

3. Results and discussion

The near infrared spectra of a few silica gel samples with varying surface area are shown in Fig. 2. The behaviour of the second derivated near infrared profiles of silica gel samples with increasing surface area is illustrated in Fig. 3. Near infrared spectra of a silica gel sample before and after drying at 200 °C under vacuum are shown in Fig. 4.

The PLS calibration loading plots for the calibration models are shown in Fig. 5. The Plots showing the measured and predicted surface area of the samples in the calibration sets are given in Figs. 6 and 7, respectively.

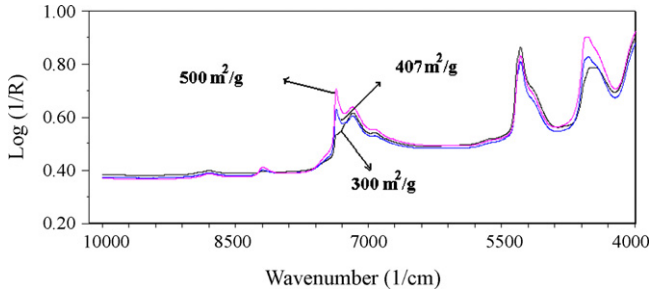

Fig. 2. Near infrared spectra of silica gel samples with varying surface area.

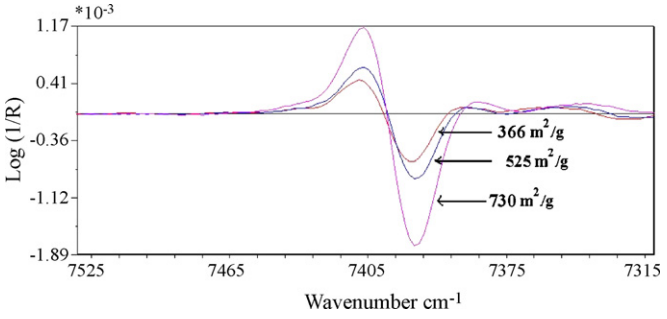

Fig. 3. Behaviour of second derivated profiles of near infrared spectra of three silica gel samples in the region 7525–7315 cm^{-1}.

Fig. 2 shows the variations in the NIR absorption profiles of the silica gel samples with surface area. Increase in the absorptions of the hydrogen bonded silanol groups at 7125 and 6875 cm^{-1} is evident in the absorption profiles. A comparison of the spectra shown in Fig. 4 indicates the evolution of the adsorption of the water molecules on silica gel surface. The water molecules form hydrogen bonds with the silanol groups and the resulting hydrogen bonded silanol groups absorb at a lower frequency, at 7125 cm^{-1}.

The partial least squares calibration models established between the second derivated NIR spectral profiles and surface area of the first set of calibration samples in the range 300–474 m^2/g needed three components to explain 98.8% of the variance in surface area. The calibration samples in the second set in the range 500–750 m^2/g also needed three components to explain 98.2% of variance in surface area. The correlations between the measured and predicted surface area are excellent with correlation coefficients 0.987 and 0.982 for the sets 1 and 2, respectively.

The loading plots plotted between the 1st loading component, the component that describes the largest variation in the derivative spectral data against wave-number are shown in Fig. 3 for samples in sets 1 and 2. The plots show how the second derivated data profiles vary with wave-number. As stated earlier an increase in the surface area results in the increase of the absorptions of the hydrogen bonded silanol groups at 7125 and 6875 cm^{-1}. It means the first component, the component that explains the largest variance in the data should reflect these changes. To understand this feature with double derivated data, one has to understand the behaviour of the second derivated profiles of the near infrared spectra of samples with increase in surface area. Second derivated profiles of the near infrared spectra of three different samples are shown in Fig. 3 for the region 7525–7315 cm^{-1}. The intensities of the profiles increase in

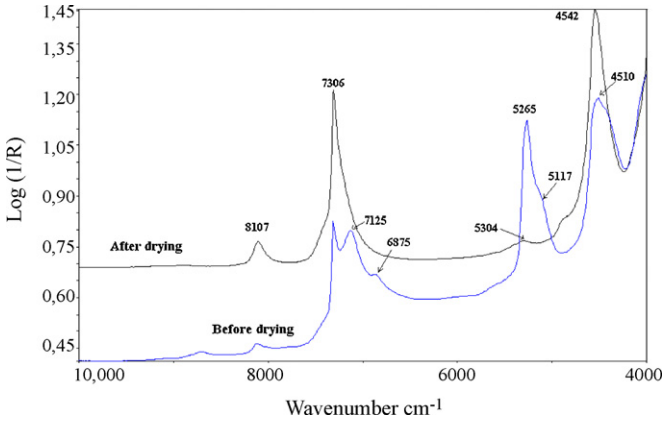

Fig. 4. Near infrared spectra of a silica gel sample before and after drying under vacuum at 200 °C.

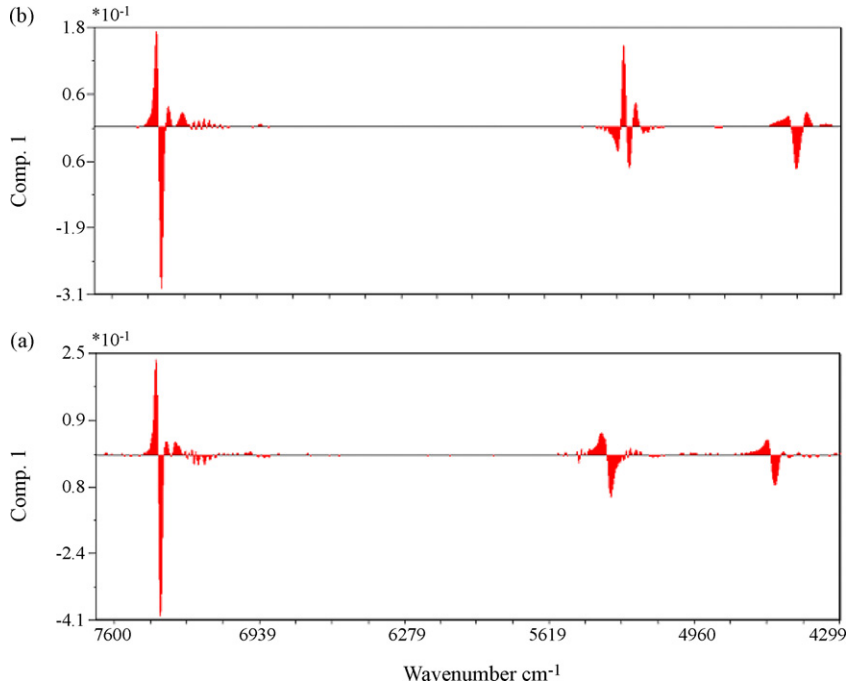

Fig. 5. The partial least squares calibration loading plots for the calibration models, (a) for calibration samples in the range 300–474 m^2/g, (b) for calibration samples in the range 500–750 m^2/g.

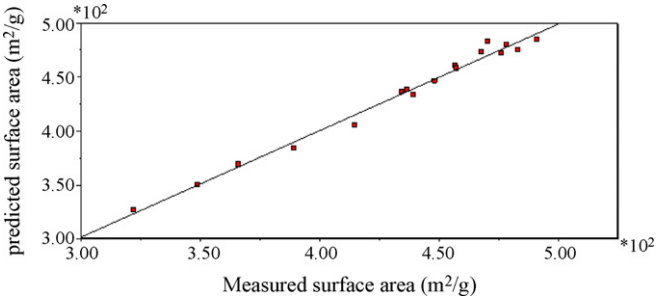

Fig. 6. Calibration plot showing the correlation between measured and predicted surface area for the samples in the range 300–474 m^2/g.

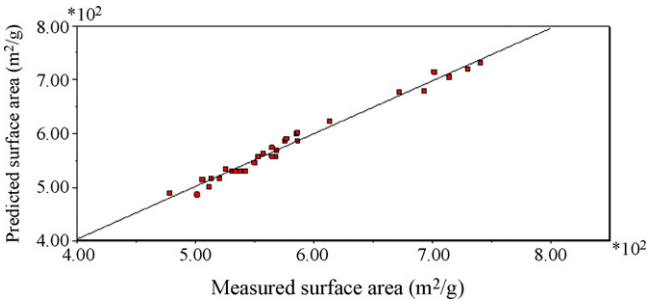

Fig. 7. Calibration plot showing the correlation between measured and predicted surface area for the samples in the range 500–750 m^2/g.

the negative direction with increase in surface area of the samples. When a multivariate calibration is carried out the first component explaining the largest variance in the spectral data will have similar profiles as shown in Fig. 3. The first loading components for the calibrations with samples in sets 1 and 2 show similar profiles and indicate that they increase in the negative direction with surface area. A similar behaviour is seen with all the peaks affected by the hydration of silica gel samples.

The calibration models established with samples in sets 1 and 2 were used to predict samples with unknown surface area. First, the near infrared spectra of the unknown samples were recorded using the same conditions as the calibration samples. The spectra were then imported into the multivariate data program and pretreated in the same manner as the calibration data set. In this case the profiles were double derivated. This process will eliminate base line effects in the spectra. The double derivated profiles are then fit in the calibration model for prediction of surface area. The mathematical process involved in the prediction and estimation of error in the prediction of unknown samples using established multivariate calibration models is detailed in ref. [16].

The prediction error in surface area for the samples in the first set was ±12 m^2/g (approximately ±2.5–4%). The error in surface area estimation carried out by using the BET method lies in the same range. The multivariate calibration models cannot predict BET surface area with a better error of prediction than the error that is inherent in the BET surface area determination by nitrogen adsorption. The prediction error in the surface area of the samples in the range 500–750 m^2/g is around ±23 m^2/g (around ±3–4.6%). This relatively high error in the surface area is reasonable because of the deviation in linearity between log (1/R) and concentration at higher concentrations. This is evident when the two sets were combined in one set and the calibration repeated. The error of prediction was around ±9%.

Table 2
Predicted and calculated surface area of the independent samples

Calibration set	Surface area predicted (m^2/g)	Surface area calculated (m^2/g)
Set 1	405	414
	436	434
	458	457
Set 2	533	525
	555	553
	719	730
	731	741

The surface area predicted for the unknown samples are shown in Table 2. There have been reports on the surface area determination of silica gel samples with error limits up to ±10%. Even though, the area predicted is acceptable, the process of multivariate calibration has given us a clear clue in this work that the surface area is better predicted with models established with samples in limited surface area ranges. Furthermore, the samples should be prepared covering the range with gradually increasing surface area.

4. Conclusion

In this paper we have demonstrated for the first time how infrared spectrometry in the near-infrared region could be used in combination with multivariate data analysis to determine the surface area of silica gel samples. The procedures used in the determinations are relatively cheap, simple, time saving and use no toxic chemicals.

The methodology demonstrated in this paper for the determination of surface area of silica gel samples removes the technical expertise one needs to determine the surface area by BET technique. Once the preliminary area measurements of the samples were made, the calibration can be carried anywhere or in any laboratory equipped with a near infrared spectrometer and the required accessory for measuring the near infrared spectra of the samples.

The application is another demonstration of the effectiveness of the multivariate PLS calibration approach in analytical chemistry. The precision of the prediction was good and the values are reliable for the purpose of characterising the unknown silica gel samples.

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